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## **PRINCIPLES AND HARDWARE OF ELECTROLYTIC CONDUCTIVITY MEASUREMENTS**

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Conductivity, Electrolytic conductivity, Resistivity, Theory, Design, Applications

### **ABSTRACT**

Electrolytic conductivity is a widely used analytical parameter in the Industrial Processing market segment. It is used throughout the "Water Cycle" ranging from water preparation, to chemical processes, to wastewater treatment. Applications include water purity analysis following ion-exchange and/or reverse osmosis units, monitoring washing and rinsing stages, chemical concentration control of dilution processes, monitoring chemical reactions, and measurement of ionic content in industrial wastewater.

Given the diversity of the applications, it should not be surprising that there is not a single measurement technology which is optimized for every situation. Rather, there are three main methodologies for electrolytic conductivity: two-electrode, four-electrode, and inductive. The classical two-electrode sensors are well positioned for measurement in high purity water and relatively low conductivity ranges. The four-electrode sensors are suited to mid to high ranges and are more resistant to fouling than two-electrode designs. The inductive sensors cover mid to very high conductivity ranges, and are particularly resistant to fouling.

This paper examines the principles of each measurement technique, the advantages and disadvantages of each, and describes specific industrial situations where each sensor type is best applied.

## INTRODUCTION

Electrolytic conductivity is one of the oldest analytical methodologies having a 200<sup>+</sup> year history. Investigating the electric shock capabilities of the torpedo fish, Henry Cavendish is credited with performing some amazingly accurate conductivity experiments dating back to 1776 [1].

Some of the reasons that this method has endured are the simplicity of the basic measurement, its low-cost, robust sensors, and the high accuracy of the technique. Further, the technology has evolved substantially since the initial findings of Cavendish to allow use in areas previous not possible. This paper will focus on on-line industrial measurement of aqueous solutions.

## THEORY OF ELECTROLYTIC CONDUCTIVITY

### TERMINOLOGY

Electrolytic conductance can be defined as the ability of a solution to carry an electric current. The conductance,  $L$  (with units of Siemens (S)), is defined as the reciprocal of the cells resistance,  $R$  (ohms) [2].

$$L = 1/R \quad (1)$$

Further, the "specific conductance" or conductivity,  $\kappa$  (units S/cm) is expressed relative to standard conditions of a fixed geometry of the electrode cell configuration. The reference conditions are for a cell with electrodes with a surface area ( $A$ ) of 1 cm<sup>2</sup> each spaced a distance ( $d$ ) 1 cm apart such that

$$\kappa = (1/R)(d/A) \quad (2)$$

Therefore, the conductivity of a solution can be determined by measuring the resistance of a cell with defined electrode geometry.

### BASIC PRINCIPLE

As illustrated in Figure 1A, the current is carried by ions dissolved in solution. Applying a potential between the two electrodes will cause positive ions to migrate toward the negatively charged electrode and negative ions to be drawn to the positive electrode. The potential applied is below activation voltage so that no reaction takes place at the electrodes [3].

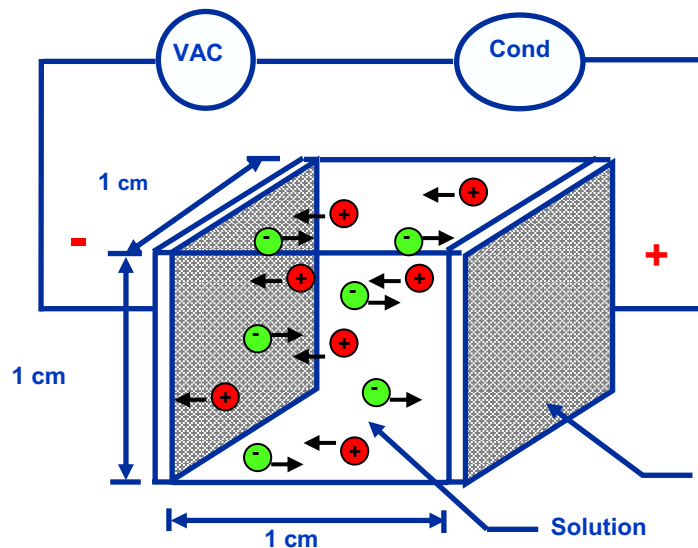


FIGURE 1A - CONDUCTIVITY CELL DESIGN

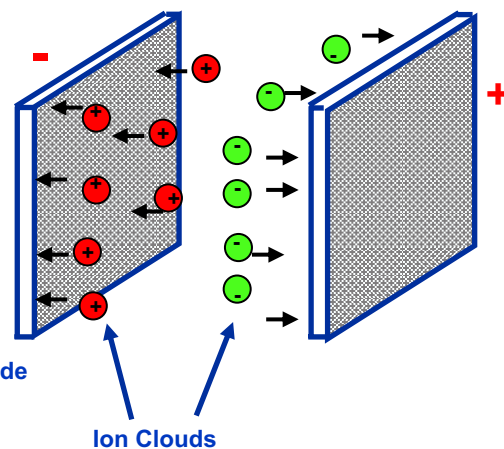


FIGURE 1B - POLARIZATION

It may be apparent from the illustration that the more ions that are available, the greater the current carrying capability. This is indeed the case in dilute solutions such that the total conductivity is the sum of the conductivity of the individual ions. The ability of the bulk solution to conduct electricity is also dependent upon the specific ions present. Each ion has a different mobility in solution, affecting its capability of carrying current. Table 1 lists the equivalent ionic conductance,  $\lambda$ , of several common ions [2]. It can be seen that the relative conductance varies substantially depending on the specific ion, with hydrogen ion and hydroxide ion being far more conductive than all other ions.

Cation	$\lambda_0$	Anions	$\lambda_0$
H <sup>+</sup>	349.8	OH <sup>-</sup>	198.6
K <sup>+</sup>	73.5	Fe(CN) <sub>6</sub> <sup>-4</sup>	110.5
NH <sub>4</sub> <sup>+</sup>	73.5	SO <sub>4</sub> <sup>-2</sup>	80.0
Pb <sup>+2</sup>	69.6	Br <sup>-</sup>	78.1
La <sup>+3</sup>	69.6	I <sup>-</sup>	76.8
Ba <sup>+2</sup>	63.6	Cl <sup>-</sup>	76.4
Ag <sup>+</sup>	61.9	NO <sub>3</sub> <sup>-</sup>	71.4
Ca <sup>+2</sup>	59.5	CO <sub>3</sub> <sup>-2</sup>	69.3
Mg <sup>+2</sup>	53.1	ClO <sub>4</sub> <sup>-</sup>	67.3
Na <sup>+</sup>	50.1	HCO <sub>3</sub> <sup>-</sup>	44.5
Li <sup>+</sup>	38.7	CH <sub>3</sub> O <sub>2</sub> <sup>-</sup>	40.9

TABLE 1 – EQUIVALENT IONIC CONDUCTANCE OF VARIOUS IONS

In consideration of all the above conditions, the conductance, L, can be expressed as [4]:

$$L = (A/d)10^{-3} \sum z_i C_i \lambda_i \quad (3)$$

Where:  $z_i$  = ionic charge of ion "i"  
 $C_i$  = molar concentration of ion "i"

One would expect conductance to vary linearly with concentration according to equation 3. While this holds true approaching infinite dilution, for many common applications, empirical correlations must be established. The conductivity response is not only non-linear at high concentrations, it can actually reach a point where additional ions will decrease the overall concentration as illustrated in Figure 2. Perhaps the most interesting example of this phenomenon is the conductivity vs. concentration curve for sulfuric acid. As shown in Figure 2, this series of peaks and troughs resembles a roller coaster more than a typical analytical calibration curve [5].

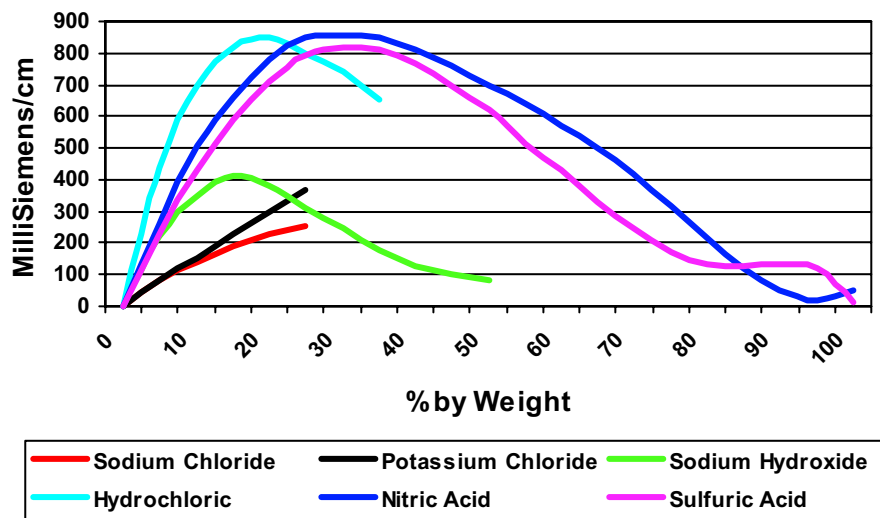


FIGURE 2 – CONDUCTIVITY vs. CONCENTRATION CURVES

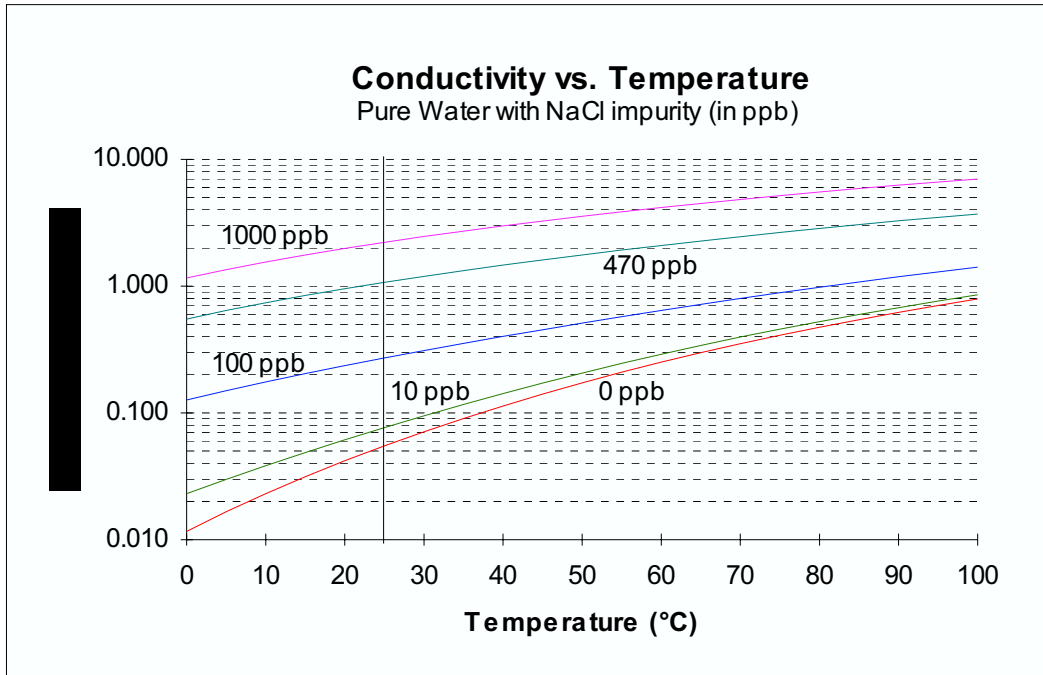
## POLARIZATION

If a DC voltage is applied, ions would build up an "ion cloud" near the surface of the electrode as shown in Figure 1B [3]. This would prevent other ions in solution from being attracted to the electrode. This is referred to as the "polarization effect". Therefore, AC potentials are utilized to prevent localized build up of ions. The AC driven signal is typically operates between 2-10 volts at 60 Hz-3,000 Hz, with lower frequencies being used for lower concentrations [2].

## TEMPERATURE EFFECTS

The effect of temperature on conductivity is a very complex relationship. An increase in temperature results in an increase in conductivity, but depending on the specific ions in solution and their concentration, the extent of the temperature effect will vary dramatically. Ultrapure water also presents an additional consideration, this being the dissociation of  $H^+$  and  $OH^-$  ions as a function of temperature. Figure 3 shows how the temperature effect varies dramatically depending both on temperature and

quality of the water [5]. Just 1 ppm (1,000 ppb) change in salt concentration changes the temperature compensation slope from approximately 5%/°C for pure water to 2.5%/°C for 1 ppm NaCl. Therefore, it is critical that all conductivity readings be referenced to a particular temperature, typically 25°C, and that the compensation factor applied is specific for the medium being measured.



**FIGURE 3 – CONDUCTIVITY vs. TEMPERATURE**

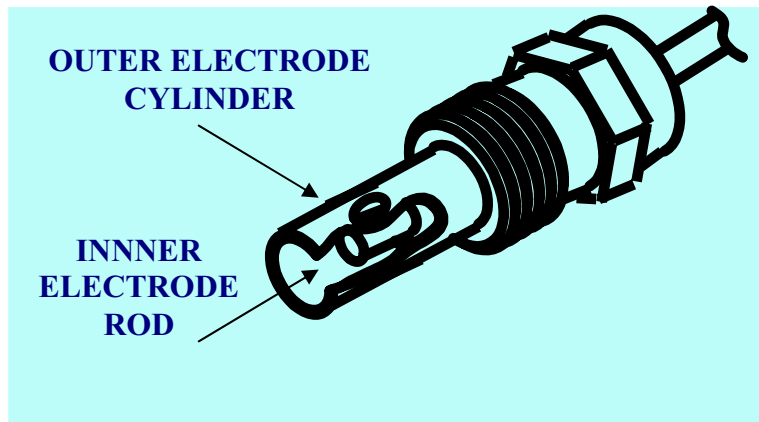
## **SENSOR DESIGNS**

### **2-ELECTRODE SENSOR DESIGN**

The 2-electrode design represents the classical conductivity measurement. Original electrodes were made of platinum, often plated with platinum black [2]. Gold was another common electrode material [3]. Today's process electrodes are typically made of titanium, graphite, or stainless steel. A common design uses concentric rod and cylindrical electrode surfaces rather than square electrodes. An example of a 2-electrode sensor for on-line use is illustrated in Figure 4.

The basic operating principle is as described above in the theory section with the exception of materials of construction and geometric configuration.

Temperature sensors are most always built into all on-line conductivity sensors, with a variety of temperature compensation algorithms appropriate to match the measured solution, selectable within the conductivity transmitter.



**FIGURE 4 – CONCENTRIC 2-ELECTRODE DESIGN**

2-electrode Sensor Considerations – The 2-electrode design excels in applications of low conductivity solutions. The well defined cell geometry and the high solution resistance allow for very accurate and precise conductivity determination.

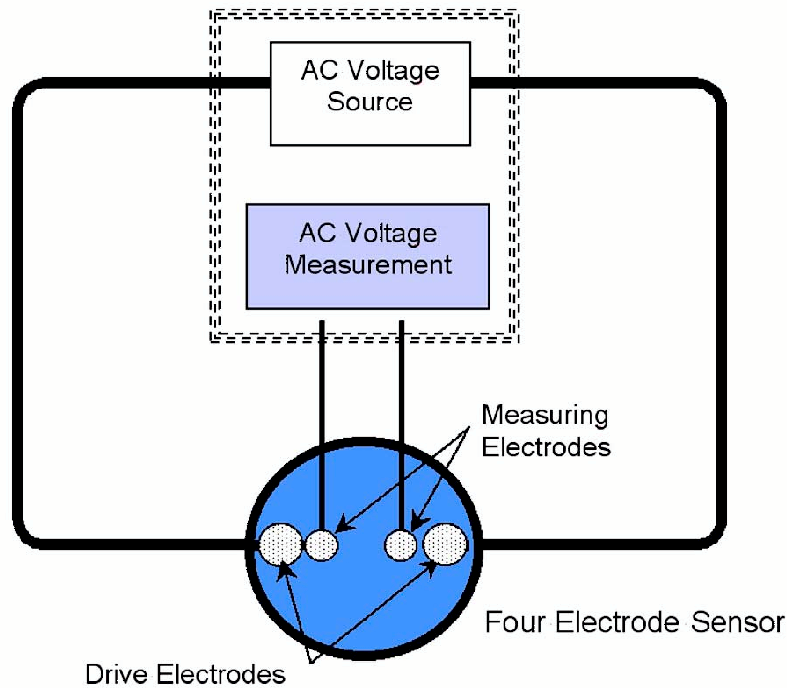
Polarization can still occur to an appreciable degree at high ionic concentrations even with the use of an AC voltage. While the range of application is dependent on the cell constant and transmitter used, 2-electrode sensors are typically applied to conductivity measurements not greater 1,000-10,000 uS/cm. Also, the cell resistance measured is the total of the solution plus any resistive coatings on the electrode surfaces. Therefore, resistive coating on the electrode surface will directly affect the reading.

#### **4-ELECTRODE SENSOR DESIGN**

The 4-electrode sensor design is illustrated in Figure 5. An AC voltage is applied across the 2 outside electrodes as with the 2-electrode sensor. However, rather than directly measuring the current between these 2 electrodes, the principle of the 4-electrode sensor is to measure the voltage drop across the 2 inner electrodes [2]. Operating with a known current condition, "I", the cell resistance can be calculated by rearrangement of Ohm's law:

$$V = I R \quad \Rightarrow \quad R = V/I$$

4-electrode Sensor Considerations – One limitation of the 2-electrode design is the polarization effect at high concentrations. In the 4-electrode configuration, there is virtually no current flow at the inner voltage sensing electrodes. Therefore, polarization does not occur, allowing the 4-electrode design to be used at higher concentrations. A second benefit of the 4-electrode sensor is its tolerance of electrode coating. Since the 4-electrode technique measures potential drop rather than resistance, the measurement remains accurate, despite minor coating. Other advantages of the 4-electrode design are its design permits easier in-process cleaning than 2-electrode designs, and that it can be installed in smaller piping than inductive sensors.



**FIGURE 5 4-ELECTRODE SENSOR DESIGN**

## **INDUCTIVE SENSOR DESIGN**

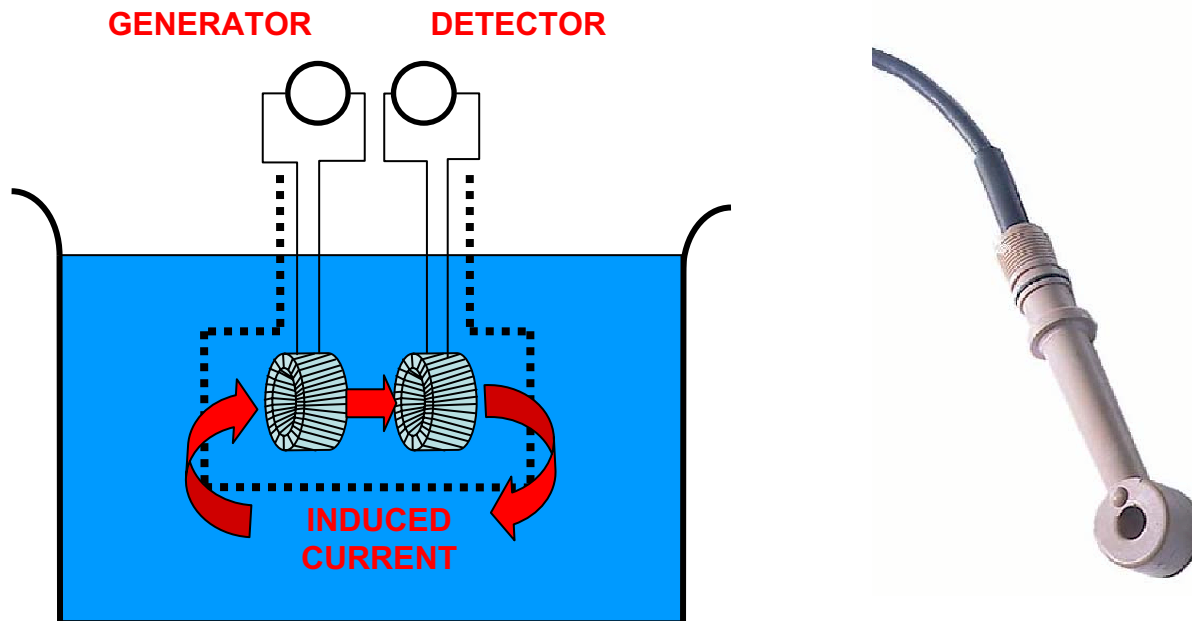
The next methodology differs substantially from the previous described methods. Due to the nature of the measurement principle, the "inductive" design is also known by a variety of names including "non-contacting" conductivity or "electrodeless" conductivity owing to the fact that there are no metallic electrodes in contact with the solution. Given the sensor construction, it is also referred to as "toroidal" conductivity.

The inductive conductivity sensor consists of two toroidal coils encapsulated in an inert polymer body (PEEK, polypropylene, etc.) as shown in Figure 6. One coil is energized at a frequency of 10 kHz - 20 kHz, which, by means of electromagnetic principle, induces an electric field through the center bore of the sensor [6, 7]. When placed in a conductive solution, a current loop is generated, which is then sensed by the measurement toroid. The more conductive the medium, the more signal is transferred to the second coil.

Inductive Sensor Considerations – The inductive design offers several major advantages over other designs: since there are no metallic electrodes contact with the sample solution, corrosion is less of an issue; there are no polarization effects; and the signal increases with decreasing resistance (as compared to opposite with contacting electrodes). Also, to a great extent, the sensor is not affected by resistive coatings on the sensor, including oils and grease.

An installation consideration is that the induced field extends several inches beyond the sensor body itself. Therefore, typically larger piping is required for inductive sensors than contacting. If sufficient clearance is not provided, the reading will be impacted. If the piping is non-conductive, the readings

will be low, if the piping is conductive, the readings will be high. This effect can be compensated by calibrating the sensor in the configuration in which it will be used.



**FIGURE 6 – INDUCTIVE SENSOR DESIGN**

## **APPLICATIONS**

### **TYPES OF APPLICATIONS**

There are two major types of applications where conductivity is used; either for detection of the presence of an impurity, or, as determination of concentration of a specific chemical.

Perhaps the largest application of conductivity is during water purification. The presence of any ionic contamination clearly can have a major impact on product as applied to semiconductor rinsing and water for injection. Impurities in water used in industrial processing can raise concerns due to reduced lifetime of resin beds, scale formation at heat exchangers and boilers, or undesirable flavors and odors in food industry.

Rinsing stages in manufacturing processes can be optimized using conductivity measurement to assure elimination of impurities while minimizing water consumption.

Another major class of applications involves determination of chemical concentration. It has been discussed that conductivity is non-specific; unable to distinguish specifically which ions are present. However, under controlled conditions, the presence of binary mixtures (1 chemical + water) is well suited for concentration measurement and control.

Some specific examples of each of these types of applications and each conductivity sensor type are presented below.

## **APPLICATION EXAMPLES**

Water Preparation for Production – High purity water plays a key role in the production of quality product across industries including chemical and industrial processing, food and beverage, and bio/pharmaceutical. Conductivity is an ideal measurement parameter for detecting trace impurities throughout the water purification stages including measuring incoming water, monitoring efficiency of ultra-filtration and reverse osmosis units or ion-exchangers. The 2-electrode sensor provides the high accuracy and sensitivity required in these installations, and there is no concern for dirty particles coating the sensor.

CIP Chemical Control – A common practice in the Food and Beverage industry is to Clean In Place (CIP) process piping and vessels by pumping sodium hydroxide through the process. Typically, bulk chemicals are stored at a high concentration, 40-45%, and then diluted to the required concentration, typically 3-5%. This represents a binary mixture of sodium hydroxide and water, and over this range, there is a significant change in conductivity (refer to Figure 2) making it a sensitive, fast responding detector. Therefore, this dilution step can be controlled by applying feedback control from a conductivity measurement system. Also, in the process lines, conductivity is commonly used for interface detection. The lines are sequentially flushed with cleaning agents, caustic, and water. Conductivity senses when the caustic is sufficiently flushed from lines and ready for process. Due the high conductivity of the caustic, a requirement for hygienic and sterilizable design, and preference to keep piping size small, the 4-electrode is the sensor of choice.

Pulp and Paper Caustic Measurement – Caustic solutions including sodium hydroxide, sodium carbonate, sodium sulfide and sodium hypochlorite are widely in the pulp and paper industry. Hydroxide ions are far more conductive than its resulting neutralized salts. Therefore, conductivity is a useful indication of sodium hydroxide concentration. Complex mixtures of chemicals minimize the application of conductivity for absolute concentration measurement. Rather, it is a valuable tool for monitoring trends in concentration of white liquor feeding digesters, recovering depleted black liquor, or monitoring fiber rinsing efficiency. Inductive sensors are required due to the high concentration range, the potential for precipitates and scaling, as well as fibers in solution.

## **CONCLUSION**

The theory and measurement of electrolytic conductivity is more complex than simply two electrodes immersed into solution. Conductivity has established a broad base of applications from ultrapure water, to chemical concentration control, to wastewater monitoring despite the fact that conductivity is non-specific. By knowing both the limitations and the capabilities of the methodology, coupled with continued advances in hardware technology, the applications of electrolytic conductivity will continue to expand over its third century of service.

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