Conductivity sensors measure a solution’s ability to conduct electricity, which is a function of all dissolved ionized solids in the solution. These detectors are packaged either as probes (with isolating valves for removal, without opening up the process) or in the flow-through designs.

**INTRODUCTION**

Conductivity analyzers measure ionic concentration of electrolyte samples. Cells and instrumentation are designed to measure the electrical resistance (or its reciprocal, the conductance)
8.17 Conductivity Analyzers

in a volume element of the electrolyte and to limit electrode–solution interfacial contributions to this measurement. A variety of sensors have been developed, some using electrodes in contact with the sample, and others not. These sensors can be combined with modern microelectronics, often with integrated software programs, which improves the quality of measurement of concentration of ionic components in process samples.

THEORY OF OPERATION

The unit of conductance, the reciprocal of the ohm, is the siemens (S). This unit impresses a measurement of the mobility or velocity of ions in an electrolyte under an imposed electric field. The value of this unit depends on the number and hence on the concentration of ions present, which provides its value in analytical measurements. However, since the mobilities of dissimilar ions are different, the measurement response provided by the cell is useful only if the detected component is the sole, or at least the major, contributor to the measured conductivity. Equivalent conductivity is defined as the conductance that is reported for one gram-equivalent weight of the conducting ion.

The mobility of ions is affected by temperature and by the total concentration of all ions in the solution. Mobility of ions and hence conductance increases with temperature (about 2% per °C) and also with dilution. Table 8.17a shows values of conductance, expressed as equivalent conductivity, of several ions at 25°C corrected to infinite dilution, together with temperature coefficients.

Figure 8.17b shows the relationship of cell geometry to the measured conductance of the solution. The electric field applied to the cell is E/d. The current density i/A is the sum of the individual charge carriers in the field, and therefore the conductivity L (which from Ohm’s law is the current divided by the voltage) is given by

\[ L = (a/d) \sum z_i c_i \Gamma_i \]

8.17(1)

TABLE 8.17a
Equivalent Conductivity of Several Ions at Infinite Dilution at 25°C (S·cm²·mol⁻¹)

<table>
<thead>
<tr>
<th>Cations (^a)</th>
<th>(\Gamma), degrees</th>
<th>Tempco, (\text{degrees} \text{ Tempco}^c)</th>
<th>Anions (^b)</th>
<th>(\Gamma), degrees</th>
<th>Tempco(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>349.8</td>
<td>0.0139</td>
<td>OH(^-)</td>
<td>198.6</td>
<td>0.018</td>
</tr>
<tr>
<td>K(^+)</td>
<td>43.5</td>
<td>0.0193</td>
<td>Cl(^-)</td>
<td>76.4</td>
<td>0.0202</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>50.11</td>
<td>0.0220</td>
<td>SO(_4)^{2-})</td>
<td>71.42</td>
<td>0.02</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>59.50</td>
<td>0.0230</td>
<td>SO(_4)^{2-})</td>
<td>80.0</td>
<td>0.022</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>53.06</td>
<td>0.022</td>
<td>CO(_3)^{2-})</td>
<td>69.3</td>
<td>0.02</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>53.6</td>
<td>0.02</td>
<td>HCO(_3)^-)</td>
<td>44.5</td>
<td>—</td>
</tr>
<tr>
<td>(n-Bu)_4N(^+)</td>
<td>19.5</td>
<td>0.02</td>
<td>Picrate(^-)</td>
<td>30.4</td>
<td>0.025</td>
</tr>
</tbody>
</table>

\(^a\)Data from reference 1.
\(^b\)Data are on an equivalent basis.
\(^c\)Tempco = (1/\(\Gamma^0\)) (d\(\Gamma^0\)/dT).

FIG. 8.17b
Simplified schematic of two-electrode conductivity circuit.

\[ L = \text{conductance in ohm}^{-1} \text{ or siemens} \]
\[ a = \text{area of electrodes in cm}^2 \]
\[ d = \text{distance between electrodes in cm} \]
\[ c_i = \text{the concentrations of the participating ions in equiv./cm}^3 \]
\[ \Gamma_i = \text{the equivalent conductivity of the participating ion in S·cm}^2\text{equiv.} \]
\[ z_i = \text{the charge on the participating ion} \]

THE CELL CONSTANT

It is not convenient to measure the ratio d/a geometrically for each cell, but since it is constant for any given cell, it may be assigned a value \(\theta\), in cm⁻¹, termed the cell constant. It is determined experimentally using solutions of accurately
known concentrations of potassium chloride, for which values of specific conductivity (the conductance of a cube of the solution, 1 cm on each side), denoted by \( k \) (in S/cm), have been precisely determined per American Society for Testing Materials (ASTM) Standard D1125–77. A few specific conductivity values are listed in Table 8.17c.

The cell constant is readily determined using the expression

\[
\theta = \frac{k}{L},
\]

where \( k \) (the specific conductivity) is known from the tabulated values, and \( L \) (the conductance) is measured using the cell being calibrated. Note that conductance and resistance are values read by measuring instruments and have the units of siemens and ohms, respectively. Conductivity and resistivity are intrinsic properties of solutions; they are obtained after application of the cell constant and have the units of siemens-centimeter and ohm-centimeter, respectively.

### Cell Dimensions

As the dimensions of the cell are changed, the cell constant varies as the ratio of \( d \) to \( a \). For solutions of low conductivity (about 0.05 to 200 \( \mu S/cm \)), the electrodes can be placed closer together, giving cell constants in the range of 0.1 to 0.01 cm\(^{-1}\). Similarly, for more conductive solutions (about 10 to 20,000 \( \mu S/cm \)), electrode separations can be increased to give cell constants of 1, 10, or sometimes 100 cm\(^{-1}\).

This has the effect of adjusting the actual conductance read by the instrument to a conveniently measured range. Signal-to-noise considerations limit resistance measurements to less than about 2 Mohm. Conductance measurements are limited by signal level magnitudes to less than about 0.2 mS.

Composition measurement using conductivity is popular in industrial process measurement and control applications, because of the inherent simplicity and reliability of the technique. Cells are available that cover a resistivity range of 1 to \( 10^8 \) in aqueous electrolytes (Figure 8.17d).

Three types of cells are used: two-electrode, four-electrode, and electrodeless. The four-electrode and electrodeless cells and their associated instrumentation are shown in Figures 8.17e and 8.17f, respectively.
Two-Electrode Cells

Two-electrode cells are best suited for measurement in clean solutions to avoid errors caused by the formation of coatings and films on the electrodes. In these designs, it is desirable to minimize the interfacial impedance of the electrodes with the solution, because the goal is to measure the bulk conductivity of the electrolyte.

Derivation of Equation 8.17(1) assumed no iR (potential) loss at the electrodes or in the leads to the cell. The cell and instrument are designed accordingly. In order to avoid significant electrolysis, a small-amplitude (usually sinusoidal) waveform having a frequency in the range of 100 to 1000 Hz is used for excitation.

In addition, the electrode materials are selected to reduce polarization or iR (potential) drops at electrode–solution interfaces. Ideally, the electrodes are made of platinum and are coated with a layer of platinum black. As the conductance of the measured solution decreases, polarization and coating effects become less significant, and metals other than platinum, such as Monel and titanium, are considered as inert electrode materials.

Particularly noteworthy is the class of two-electrode conductivity applications, called resistivity measurements, which employ titanium two-electrode cells in monitoring the high-purity water used in semiconductor manufacturing, steam turbine applications, and nuclear reactors.

Four-Electrode Measurement

Four-electrode conductivity is useful for high conductance when coating and fouling of electrodes are a concern. Current is imposed across two drive electrodes, and the potential drop through the electrolyte is detected between two points in the cell using two sense electrodes (Figure 8.17e). The sense electrodes are monitored with a high-input impedance, voltage-measuring amplifier to minimize the current drawn and electrode polarization.

Polarization at the drive electrodes has no effect on the measurement, provided the drive voltage is able to maintain the control current through the cell. This voltage increases with fouling and can be used as a diagnostic tool to signal the user when cleaning is required.

Because of geometrical considerations, four-electrode designs are not suited to probe configurations. Precise measurements require flow-through cells that allow linear distribution of current across the sense electrodes. When used in probes, four-electrode measurements are best applied to setpoint control.

Typical applications include measurement of salts, acids, and alkalis in chemical processes in the mining, metallurgy, pulp and paper, and aluminum industries, where samples often contain solids, oils, or other materials that form insulating coatings on the electrodes.

Electrodeless Cells

One way to eliminate electrode polarization effects is to eliminate the electrodes. Techniques to do this are referred to as electrodeless conductivity measurement or, alternately, as inductive or toroidal sensing of conductivity. The probe shown in Figure 8.17f consists of two encapsulated toroids. When immersed in the electrolyte, the solution forms a conductive loop shared by both toroids. One toroid radiates an electric field in this loop, and the other detects a small, induced electric current. Practically speaking, the two toroids form a transformer whose coils are interconnected by the resistance of the electrolyte.

The radiated field is typically 20 kHz, and the induced current, which is proportional to the conductivity, is amplified, rectified, and displayed. These probes are encapsulated in nonconductive, temperature-stable, and chemically resistant materials such as the fluorocarbon polymers.
MEASUREMENT APPLICATIONS

Modern conductivity analyzers, with on-board computers, provide essential features such as temperature correction to reference values, digital display of concentration data from measured values, controller functionality, self-diagnostics, and calculations such as water subtraction and percent rejection.

Concentration Measurements

Temperature compensation and concentration computation data for common acids, bases, or salts are often imbedded in the instrument’s software. Data for less common materials may often be loaded by the end user. Concentration can be derived from the conductivity of an electrolyte, when there is a significant increase or decrease in conductivity with increasing concentration.

While concentration measurements are most often applied to a single electrolyte in solution, they can also be applied to mixtures of electrolytes, when the ratio of the components of the mixture is constant. Concentration measurement is also used in batch reactions, where the progress of the reaction is accompanied by a significant increase or decrease in conductivity. Output signals, either digital or analog, are used in control systems for measurement and control of such processes as boiler feed water or the monitoring of gas scrubber solutions, pickling and plating liquors, etc.

High-Purity Water Measurements

A special class of temperature compensation has evolved for measuring high-purity water. Monitoring of high-purity water is used in semiconductor processing. In power and pharmaceutical applications, it is necessary to distinguish the temperature coefficient of pure water from that of ionic purity.

Today’s “intelligent” instruments can measure both conductivity or resistivity and temperature. They can therefore compute the value of conductivity or resistivity of pure water at the measured temperature. They can also calculate the measurement contribution due to the impurities and output the conductivity or resistivity of the process water, referenced to a standard temperature, or the concentration of impurity after subtraction of the contribution due to the water (for example, as total dissolved solids (TDS) or particles per million (ppm) NaCl).

Multiple sensors are used in conjunction with ion exchange columns or reverse osmosis systems to monitor and control inlet and outlet resistivity across the bed and the breakthrough of unwanted ions and, as a predictive tool, to signal the need for bed regeneration. If the sample temperature is not controlled, water temperature compensation is necessary for accurate measurements for conductivity values at or below 1 \( \mu \text{S/cm} \), or resistivity readings at or above 1 Mohm-cm. A variant of this temperature compensation, called cation conductivity temperature compensation, is used for high-purity water samples, such as the effluent of a cation exchange bed, which has acid as the major impurity.

Corrosive and Fouling Applications

The other extreme, i.e., highly conductive solutions—those that are highly concentrated, corrosive, and contaminated with fouling materials—is best measured with the electrodeless designs. Here, coatings only affect the measurement response to the extent that they alter the geometry, and hence the cell constant, of the probe. The relatively large size of these probes renders this effect small or negligible. Examples of applications include on-line analysis of oleum in \( H_2SO_4 - SO_3 - H_2O \), measurement and control of alkalinity and solution strength in many industries using lime slaking, industrial dishwashing rinse control, gas scrubber solution concentration control, and many others.

Pulp processing uses extremely corrosive chemicals, high temperatures and pressures, and samples entrained with solids and particles; such processing provides an example of how conductance analyzers are applied. Figure 8.17g shows how the conductivity sensors are integrated into a continuous Kraft digester commonly used in paper pulp making.

Temperature, flow, and alkali concentration data are used by the control systems to control the uniformity of the pulp by manipulating the residual alkali strength in the cooking liquor in response to such changing feed properties as wood chip composition, species, chip moisture, and uniformity of concentration of makeup chemicals. For a summary of conductivity analyzer applications, refer to Table 8.17h.

Fig. 8.17g
Example of conductivity measurement used in control of batch digester for paper making.
8.17 Conductivity Analyzers

**CALIBRATION AND MAINTENANCE**

**Calibration of Conductivity Sensors**

Conductivity measurements can be calibrated using conductivity standards or on-line, by grab sample analysis. The conductivity sensor should be given sufficient time to reach the temperature of the standard solution, or in the case of on-line calibration, the sensors should be calibrated only after the process has been at a stable temperature for some time. By so doing, temperature compensation errors are eliminated, because the temperature element in the conductivity sensor will have had time to reach the same temperature as that of the standard or the process. This is especially important when using electrodeless sensors, which typically have a much larger mass than contacting sensors, and therefore require more time to reach thermal equilibrium.

Conductivity or resistivity measurements in high-purity water applications cannot be calibrated by using standards or calibrated on-line by using grab samples. This is because of the extreme sensitivity of the samples to contamination by trace amounts of electrolytes and even to atmospheric CO₂. It has been argued that the accuracy of calibrations, when using conductivity standards of less than 100 µS/cm, can be questionable.

Therefore, the conductivity sensors on high-purity water applications should be calibrated by calibrating the input to the analyzer with precision resistors (usually done by the manufacturer) and using a conductivity sensor with a predetermined cell constant, which is then entered into the software of the analyzer by the user. Further calibrations are done using a certified reference conductivity system.

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**TABLE 8.17h**

**Conductivity Applications**

<table>
<thead>
<tr>
<th>Process</th>
<th>Application (Usage) and Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical streams</td>
<td>To measure and control solution strength.</td>
</tr>
<tr>
<td>Steam boilers</td>
<td><strong>Blowdown</strong> is a method of lowering the amount of dissolved solids in a boiler by dilution. To control buildup of dissolved solids to prevent scaling and corrosion.</td>
</tr>
<tr>
<td>Condensate return</td>
<td><strong>Condensate return</strong> is usually checked for quality before being returned to the boiler. If out-of-limits, it is dumped.</td>
</tr>
<tr>
<td>Waste streams</td>
<td>A means of determining the amount of dissolved salts being discharged.</td>
</tr>
<tr>
<td>Cooling towers</td>
<td><strong>Bleed control</strong> is a method of reducing the total dissolved solids in a tower by dilution (similar to blowdown). To prevent scaling and corrosion. For bleed control, the electrodeless conductivity system works best to minimize maintenance and failure.</td>
</tr>
<tr>
<td>Fruit peeling</td>
<td>Strong caustic is used, and its strength can be determined by conductivity.</td>
</tr>
<tr>
<td>Rinse water</td>
<td>Plating shop running rinse water is monitored for dissolved salts—a method of reducing water consumption.</td>
</tr>
<tr>
<td>Semiconductor rinse water</td>
<td>Requires ultrapure water, usually measured in mega-ohms/centimeter.</td>
</tr>
<tr>
<td>Interface determination</td>
<td>Usually used in food processing, e.g., dairy and brewing. Most commonly used in cleaning in place (CIP); interfaces in pipes are easily determined and can be diverted by valves controlled by conductivity.</td>
</tr>
<tr>
<td>Demineralizer output</td>
<td>Determination of ion exchange exhaustion.</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Efficiency of reverse osmosis (RO) operations is usually monitored by comparing inlet and outlet conductivity or TDS ratio (cell 1/cell 2). The inlet conductivity is installed upstream of the RO feed pump to avoid high-pressure requirements. Also, abnormal readings can be used to diagnose membrane fouling, improper flow rate, membrane failure, etc.</td>
</tr>
<tr>
<td>Desalination</td>
<td>Similar to reverse osmosis and demineralization process.</td>
</tr>
<tr>
<td>Deionization process</td>
<td>Conductivity or resistivity measurement provides capability for monitoring and controlling the acid and caustic dilution. Regeneration of deionizers requires consistent application of acid and caustic to obtain repeatable results. Savings is provided by consistent regeneration, which assures deionized water availability, less frequent regeneration, long resin life, and conservation of costly reagents. More precise control can be obtained by using conductivity ratio measurement. A comparison of inlet and outlet (ratio of cell 1/cell 2) conductivity across the bed can determine the unwanted ions and the need for bed regeneration, which can compensate and control for variations in mineral concentration of feed water.</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Occasionally loses resin. If a resin bead or fines are trapped between the electrodes of a cell, it is shorted and produces a very low resistivity (or high conductivity) reading. This feature is a great help in troubleshooting.</td>
</tr>
</tbody>
</table>
Maintenance of Conductivity Cells

Conductivity measuring systems may be designed to be trouble-free and produce reliable measurements; however, some maintenance is required, especially for the electrodes. In addition, the cell may require periodic cleaning depending on the type of application, the quality of the water passing through it, and the type of cell used. Some types of contaminants may not interfere directly with the measured conductivity—e.g., organic materials, rust, and suspended solids—but may form deposits on the electrode surfaces. In most cases, these surfaces can be cleaned with a bristle brush and a weak detergent solution.

Problems may also occur in hard-water applications, where gradual formation of scale will reduce the active area of the electrodes, which over a period of time will result in an apparent decrease in conductivity. For this type of fouling, simple brush cleaning is insufficient, as it will not remove scale from the cell. To remove the scaling, the electrode should be treated with a 10% solution of formic or hydrochloric acid. The presence of bubbles will indicate that the scale is being dissolved. It takes about 2 or 3 min and is complete when the bubble formation ceases. Then the cell should be thoroughly rinsed to remove all traces of acid before it is returned into the process.

Cells with stainless steel electrodes are generally used in applications where a low conductivity is combined with low concentrations of organic contamination. For high-purity water applications, titanium electrodes are used, because of their better performance characteristics in very low conductivity samples.

In applications where fouling or corrosion is anticipated, the need for cleaning can best be minimized by the use of electrodeless conductivity sensors.

CONCLUSION

Selecting the right conductivity cell includes having information on the cell constant for the analyzer, the conductivity range, the materials of construction selected to resist corrosion, and the appropriate mounting of the sensor.

When designing a conductivity measurement system, the first consideration is the conductivity range of the sample. In applications up to 20,000 µS/cm, typically contacting conductivity sensors are used. For higher conductivity ranges, or in samples that can foul or corrode the metal electrodes, electrodeless detectors are the best choice.

For conductivity measurements at 1 µS/cm and below, contacting conductivity sensors should be used in conjunction with a conductivity analyzer, which is provided with high-purity temperature compensation.

References


Bibliography