23

CONDUCTIVITY ANALYZERS AND THEIR APPLICATION

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23.1 THEORY OF ELECTROLYTIC CONDUCTIVITY

23.1.1 Background

Conductivity measurement has widespread use in industrial applications, which involve the detection of ionic contaminants in water and concentration measurements. Conductivity measures how well a solution conducts electricity.

The units of conductivity are siemens per centimeter (S/cm), which is identical to the older unit of mho/cm. Conductivity measurements cover a wide range of solution conductivity from pure water at less than 1×10^{-7} S/cm to values in excess of 1 S/cm for concentrated solutions (Fig. 23.1). For convenience, conductivity is usually expressed in the units of microSiemens/cm (µS/cm, one-millionth of a S/cm) or mS/cm (mS/cm, one-thousandth of a S/cm).

In certain industries, the conductivity of water approaching purity is measured in terms of its resistivity. The units used are megohms-centimeters ($\mathrm{M\Omega \cdot cm}$), where 18.3 $\mathrm{M\Omega \cdot cm}$ is the resistivity of pure water at 25°C. In many of these applications, a minimum resistivity value is used as a criterion for acceptability of the water sample.

23.2 CONDUCTIVE SOLUTIONS

Conductivity is measured primarily in aqueous solutions of electrolytes. Electrolytes are solutions containing ions, which are charged particles formed by

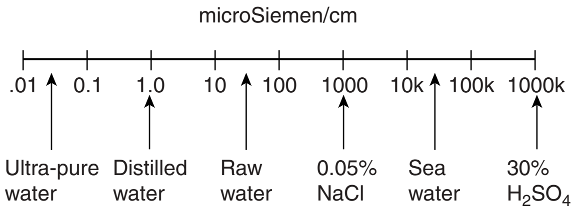


Figure 23.1 Conductivity of common samples.

the dissociation of acids, bases, salts, and certain gases such as carbon dioxide, hydrogen chloride, and ammonia. Water is the solvent in virtually all electrolyte solutions, because water is one of the rare solvents that has the capability of stabilizing the ions formed, by a process called *solvation*. Pure water itself can conduct electricity, because it dissociates to form hydrogen ion (H^+) and hydroxyl ion (OH^-). In the range of common industrial conductivity measurements, solutions made with organic solvents and water solutions made with nonelectrolytes (like alcohol) are only sparingly conductive and are, for the most part, considered nonconductive.

Conductivity is nonspecific. Electric current can be carried in a solution by any ions present. As a result, conductivity measurements respond to any and all ions present in a solution. All that can be said about a conductive solution is that it contains ions. An electrolyte in a solution cannot be identified, or its concentration known from conductivity alone. To determine concentration with a conductivity measurement, the user must have additional information about the solution.

23.3 CONCENTRATION DEPENDENCE OF CONDUCTIVITY

Since ions are the charge carriers in a conductive solution, it would be expected that the higher the concentration of ions in a solution, the more conductive it would be. While this is true for dilute solutions and also for certain electrolytes up to their saturation point, ion–ion interactions in the solution can cause the conductivity response to deviate considerably from what would be expected to be a linear response.

In very dilute electrolyte solutions, with conductivity below 10 μS/cm, ions behave independently, so the conductivity response with increasing concentration is essentially linear. In this low range, the conductivity of a mixture of electrolytes is pretty much the additive sum of their individual conductivities, barring any reaction between them.

Above 10 μS/cm, ion–ion interactions become significant greater as the concentration increases. The conductivity response with increasing conductivity is progressively nonlinear. Some electrolyte solutions can even reach a maximum conductivity in the percent by weight concentration range, after which there is a decrease in conductivity with increasing concentration. This makes the task of deriving concentration from conductivity measurements highly dependent on the conductivity behavior of the electrolyte of interest.

Mixtures of electrolytes, in concentrated solutions, will exhibit conductivity less than the sum of the conductivities of their components in pure solution. How much the conductivity deviates from a simple sum depends on the electrolytes in the mixture, so no simple, general model can be developed for mixtures of electrolytes. As a result, meaningful concentration information for electrolyte mixtures cannot be obtained from conductivity measurements.

23.4 CONDUCTIVITY MEASUREMENT TECHNIQUES

23.4.1 Electrode Conductivity

Electrode conductivity uses a sensor with two metal or graphite electrodes in contact with the electrolyte solution. An alternating-current (AC) voltage is applied to the electrodes by the conductivity analyzer, and the resulting AC current flowing between the electrodes through a volume of solution is used to determine the conductance of the sensor (Fig. 23.2)

23.4.1.1 Probe Constant. The amount of current that flows depends not only on the solution conductivity but also on the length, surface area, and geometry of the sensor electrodes. The probe constant (also called "sensor constant" or "cell constant") is a measure of the current response of a sensor to a conductive solution, due to its dimensions and geometry. Its units are cm^{-1} (reciprocal centimeters; length divided by area). The probe constant scales the response to a given conductivity range to the input circuit requirements of a particular conductivity analyzer. Probe constants can vary from 0.01 to $50\,\text{cm}^{-1}$ and, in general, the higher the conductivity, the greater the probe constant necessary.

23.4.1.2 Characteristics of Electrode Conductivity. By choosing the appropriate cell constant, electrode conductivity can measure down to pure water conductivity, and even below in some special applications with organic solvents. By choosing a large cell constant, contacting conductivity can be used to measure highly conductive solutions. But there are drawbacks to using contacting conductivity in highly conductive solutions.

The main drawbacks are that the electrode sensor's susceptibility to coating and corrosion and the fact that many strong electrolyte solutions are corrosive and tend to contain undissolved material that can coat the sensor. Coating or corrosion on the

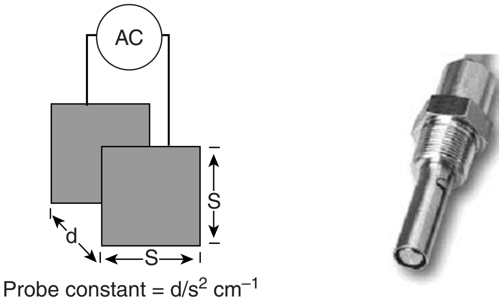


Figure 23.2 Apparatus for measuring electrode conductivity.

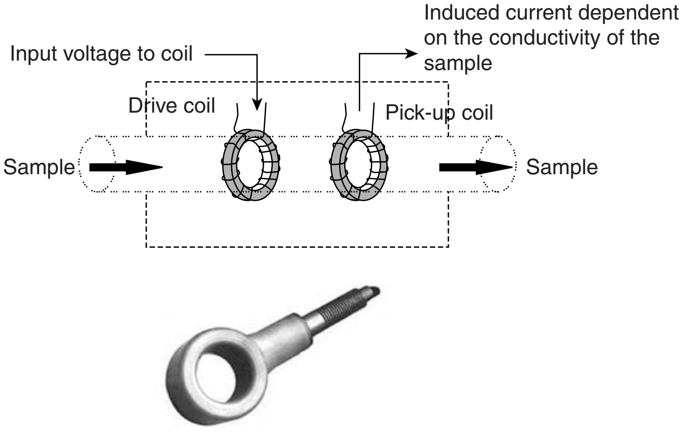


Figure 23.3 Apparatus for measuring toroidal (inductive) conductivity.

surface of an electrode lowers its effective surface area, decreasing its probe constant, and lowering the reading. The conductivity reading will decrease in proportion to the fraction of the surface area of the sensor that is coated or corroded. In strongly conductive solutions, there can also be polarization effects, which result in nonlinearity in the measurement.

23.4.2 Toroidal (Inductive) Conductivity

Toroidal conductivity measurements are made by passing an AC voltage through a toroidal coil, which induces a current in the electrolyte solution. This induced solution current, in turn, induces a current in a second toroidal coil in the sensor. The amount of coupling between the two coils is proportional to the solution conductivity (Fig. 23.3).

23.4.2.1 Characteristics of Toroidal Conductivity. The major advantage of toroidal conductivity is that the toroidal coils are not in contact with the solution. They are either encased in a polymeric material or external to the solution, as is the case with a flowthrough sensor. The toroidal sensor can be completely coated by a solid or oily contaminant in the process, with essentially no decrease in the reading until the coating builds up to a thickness of 1 cm. The polymeric material housing the toroids, or the pipe material in a flowthrough configuration, can be chosen to be resistant to corrosive solutions, which would quickly corrode contacting sensors with metal electrodes.

The major drawback to the toroidal conductivity measurement has been its lower sensitivity compared with contacting conductivity, and, although some recently (as of 2003) developed toroidal conductivity analyzers can measure low conductivity, their application has been restricted to those rare applications where the process has low conductivity and is fouling.

Toroidal sensors are also typically larger than contacting sensors and the solution current induced by the toroid occupies a volume around the sensor. So toroidal sensors need to be mounted in a larger pipe than a contacting sensor. If the toroidal sensor is mounted less than a sensor diameter from a conducting pipe, there can be an upscale reading from conduction through the pipe. Near a nonconductive (plastic) pipe, the readings can be low because of a reduction in the conductive solution volume near the sensor. Both of these effects can usually be corrected for, by zeroing the measurement loop with the sensor mounted in the dry process pipe.

23.4.3 Criteria for Choosing the Conductivity Measurement Technique

General rules for choosing the conductivity measurement technique can be outlined as follows:

- If the process is dirty or corrosive, toroidal conductivity is the only choice. An electrode conductivity sensor will require frequent maintenance, and may require frequent replacement if chemically attacked (Fig. 23.4).
- If a conductivity measurement below 10 μS/cm is required, electrode conductivity is the best choice, not only for its sensitivity but also because electrode conductivity analyzers have the features that support conductivity measurements in this range. Toroidal conductivity should only be considered for use in this range, if the potential for fouling is a major concern. The toroidal analyzer may not have the features to provide a highly accurate reading in very low-conductivity samples.
- Toroidal conductivity is generally favored for applications above 20,000 μS/cm, and it is favored, by some for applications above 5000 μS/cm, because of its lower maintenance requirements.
- Below 5000 μS/cm either toroidal or electrode conductivity can be used. Toroidal sensors are favored because they rarely require cleaning in a reasonably clean application. Electrode sensors are typically smaller and easier to install than toroidal sensors.

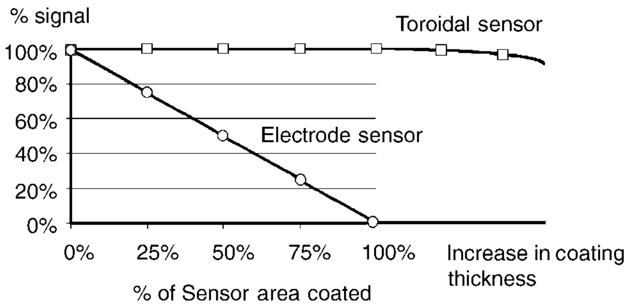


Figure 23.4 Toroidal versus electrode sensors in conductivity measurement.

23.5 EFFECTS OF TEMPERATURE ON SOLUTION CONDUCTIVITY

The conductivity of a solution always increases with temperature, due to the higher mobility of the ions, which carry the electric current. However, a solution's change in conductivity with temperature depends on the conductivity range and the identity and concentration of the electrolyte.

Online measurement of conductivity seeks to determine the concentration of a particular electrolyte, or measure the bulk concentration of electrolytes in the solution. The conductivity, reported by a conductivity analyzer, must be independent of temperature, or else a temperature increase could be mistaken for a concentration increase. As a result, all conductivity analyzers include a temperature compensation routine, which corrects raw conductivity for temperature, using a temperature element in the conductivity sensor. In most cases, the conductivity is corrected to the value it would have at 25°C, but in certain applications a higher reference temperature is used. For accuracy, the temperature compensation routine must match the temperature behavior of the solution. The three common types of temperature compensation will be examined.

23.5.1 Temperature Compensation of Moderately Conductive Solutions

In moderately ($>10\,\mu$S/cm) and highly conductive solutions with a constant electrolyte concentration, the increase in conductivity with temperature is assumed to be linear, and can be compensated for using a linear equation. This temperature compensation is termed *straight-line* temperature compensation and uses a temperature coefficient (z), which is the percent increase in conductivity per degree centigrade: $C(25°\mathrm{C}) = C(T) / [1 - z(T-25)]$, where $C(25°\mathrm{C})$ is the conductivity at 25°C, $C(T)$ is the conductivity at some temperature T, and z is expressed as a fraction.

The temperature coefficients of the following electrolytes generally fall in the ranges shown below:

Acids	1.0–1.6%/°C
Bases	1.8–2.2%/°C
Salts	2.2–3.0%/°C
Fresh water	2.0 %/°C

In some conductivity analyzers, the temperature coefficient is assumed to be 2.0%, and only that value is provided.

Finding the temperature coefficient for a particular electrolyte in the published literature can be difficult, simply because there is not a great deal of published data on temperature coefficients. The easiest alternative is to measure the change in conductivity from 25°C to the process temperature in the laboratory, and backcalculate the temperature coefficient from the equation in the preceding paragraph.

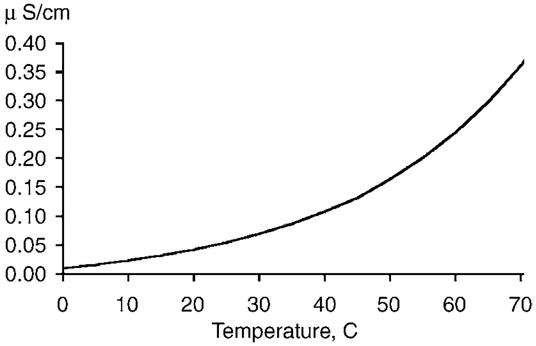


Figure 23.5 Exponential increase in conductivity with increase in temperature.

Alternately, the temperature coefficient in the analyzer can be adjusted until the conductivity reading of the warm solution is the same as it was at 25°C. Some microprocessor-based analyzers have a built-in software routine for doing this determination.

23.5.2 Temperature Compensation in High-Purity Water

In solutions with a conductivity of 1 μS/cm or less, the conductivity increase with temperature is highly nonlinear. This occurs because the conductivity of water itself is a large fraction of the overall conductivity. The ions carrying charge in water are hydrogen (H^+) and hydroxyl (OH^-) ions from the dissociation of water. With an increase in temperature, not only are the hydrogen and hydroxyl ions more mobile, but water dissociates more, so there are more ions to carry the charge. This double effect causes the conductivity to increase exponentially (Fig. 23.5). Large errors can result from using linear temperature compensation in these applications (Fig. 23.6).

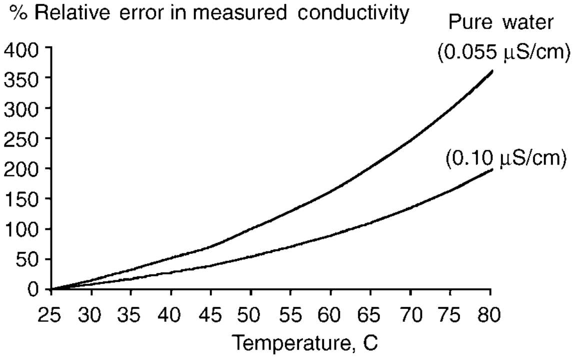


Figure 23.6 Error resulting from linear temperature compensation.

Temperature compensation for these solutions must take into account not only the increase in the conductivity of water but also the increase in conductivity of the solute (dissolved electrolyte). From pure water at 25°C (0.055 μS/cm) to 1.0 μS/cm, the fraction of the total conductivity due to the solute increases, and so the temperature compensation must also take into account the accompanying change in temperature behavior. The increase in the conductivity due to the solute will also depend on what type of electrolyte is present (i.e., acid, base, or salt).

Two major types of temperature compensation address the bulk of high-purity water applications. The first, salt temperature compensation, assumes that the small concentration of solute is salt (NaCl) and is used for most high-purity water applications. The second, more specialized compensation, termed *cation* temperature compensation, addresses applications where the solute is acidic. It gets its name from the fact that the effluent from a cation demineralizer bed, which replaces cations with hydrogen ions, is acid. This type of temperature compensation assumes that hydrochloric acid (HCl) is the solute. Other temperature compensation routines have been developed for more specialized applications, such as pure water containing a sizeable fraction of isopropyl alcohol for use in the electronics industry.

Both temperature compensations involve highly nonlinear mathematical routines, and thus are available only in microprocessor-based analyzers. Before the advent of microprocessors, the temperature of the sample was conditioned to 25°C or a portion of the compensation curve was approximated using resistor networks.

23.5.3 Temperature Compensation in Strongly Conductive Solutions

The temperature coefficient not only varies among electrolytes but can also vary over a wide concentration range of a single electrolyte (Fig. 23.7). This behavior is especially apparent when a concentrated solution of a single electrolyte is being measured. Linear temperature compensation cannot accurately address the

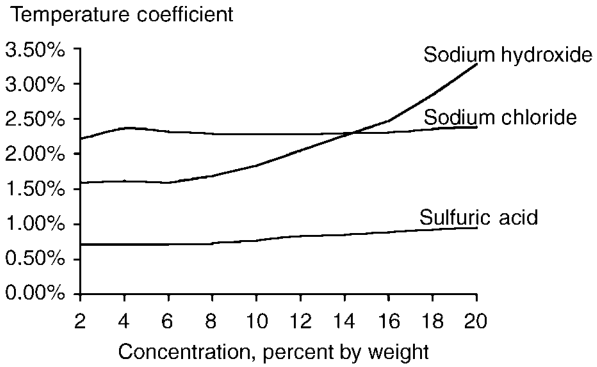


Figure 23.7 Variation of temperature with electrolyte concentration.

temperature behavior over the entire concentration range, and so a compromise is the only solution. In most cases, this means using the temperature coefficient of the concentration at the control point or alarm point, so as to maximize the accuracy at and near this point.

Changes in the temperature coefficient with concentration pose a special problem for conductivity analyzers designed to read out the concentration of a particular electrolyte. For an accurate reading over the full concentration range, temperature compensation at each concentration has to be addressed. This is usually accomplished by building the temperature compensation into the mathematical routine used to derive concentration from conductivity.

23.6 CONDUCTIVITY SENSOR MOUNTING

23.6.1 Sensor and Analyzer Locations

The conductivity analyzer should be mounted in an easily accessible location with the sensor nearby. Conductivity sensors can generally be can be located 100 m or more from the analyzer, but long distances between the sensor and the analyzer make maintenance and calibration inconvenient for a single operator, or require two operators, and some type of remote communication.

23.6.1.1 General Sensor Mounting Considerations. Conductivity sensors may be mounted in a number of ways, as will be seen, but in all cases the following points should be considered:

1. The sensor should be mounted so as to receive a continuous flow of a sample representative of the process solution. Air entrapment in the piping in the vicinity of the sensor must be avoided, as it can cause low or noisy readings.
2. The sensor (and analyzer) should be mounted in a location that allows convenient access for maintenance and calibration.
3. If there is reagent being added to the process, the sample should be well mixed before reaching the sensor. If the sensor is mounted in a vessel, good agitation is necessary to avoid large lag times in the measurement.
4. The pressure limitations of the conductivity sensor should not be exceeded. Locate the sensor at a point of lower pressure, or if this is not possible, a sidestream should be taken off the process with pressure reduction. This is also a safety issue.
5. Likewise, temperature limitations should not be exceeded. Processes with very high temperatures or temperatures in excess of the limits of the sensor should be provided with a sample sidestream and cooling. This is also a safety issue.
6. For installations in hazardous areas, it is best to use an analyzer (usually a two-wire transmitter) designed for use in the hazardous area, rather than a

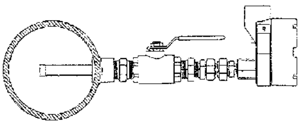
long cable run from the sensor to an analyzer in a nonhazardous area. If more information than simply a conductivity measurement is required from the analyzer, use a smart conductivity analyzer.

7. In processes where there is a potential for coating, a toroidal sensor should be used. In vessels, the sensor should be located to avoid regions where there is settling of precipitates or debris.

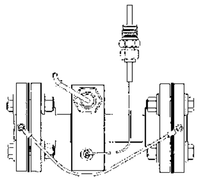
23.6.2 Mounting Configurations

The mounting configuration of a conductivity sensor is determined by the requirements of the process piping and vessels, and other considerations such as the need for sample cooling or pressure reduction. Regardless of the mounting configuration used, air entrapment in the process near the sensor is a major source of error and has to be avoided at all costs (Fig. 23.8).

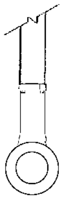
23.6.2.1 Submersion Mounting. Submersion mounting involves immerson of the sensor in a process vessel or pond on a length of conduit. It is typically used only when only access to the process is from the top. It is the most inconvenient mounting configuration for the operator, because both the sensor and its conduit must be removed for maintenance and calibration. Care has to be taken to ensure that a watertight seal is made between the sensor and the conduit, and backfilling the conduit is advisable to avoid leakage of the process into the cable end of the sensor, which causes short circuits. Because of the difficulties accessing the sensor, submersion applications are best served by toroidal conductivity, due to their lower maintenance requirements.



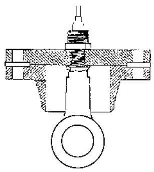
Retractable (electrode)



Flow through (toroidal)



Submersion (toroidal)



Insertion (toroidal)

Figure 23.8 Mounting configurations for a conductivity sensor.

23.6.2.2 Insertion Mounting. This configuration generally involves mounting the conductivity sensor in a tee or in through the side of a vessel. A threaded electrode sensor can simply be screwed into a pipe tee, without the need for additional hardware. Toroidal sensors are most often inserted using a flange or some manner of insertion fitting because of their larger size.

23.6.2.3 Retraction Mounting. One shortcoming of insertion mounting is the need to shut down the process or drain a vessel in order to remove the sensor for maintenance. This shortcoming is overcome using retraction mounting, which is an insertion type of mounting using a ball valve or some other isolating valve that allows the sensor to be removed while the process is running. With this configuration, the sensor can be quickly removed for cleaning, or replacement in the event of a catastrophic failure, minimizing the downtime of the conductivity measurement during the process. But it should be noted that if the conductivity range permits, using a toroidal sensor with insertion mounting is often preferable to using a contacting sensor with retraction mounting, if the purpose of the retraction mounting is simply to facilitate cleaning.

The process pressure is an important safety consideration in retraction installations. With ball-valve-type insertion devices using manual insertion and retraction, the maximum rating for the device should be strictly observed, to avoid the sensor from being ejected from the device and the operator being sprayed with the process. Inserting the sensor into the process against the force of a pressurized sample can be difficult. In cases where excessive pressure is possible but access to the sensor during running is necessary, a retractable device other than a ball valve, or a sample sidestream with pressure reduction should be chosen over a manually operated ball valve.

23.6.2.4 Flowthrough Mounting. A flowthrough configuration can be a sensor specially designed for flowthrough mounting with flanges or female threads to mate with process piping, or it can simply be a insertion or retractable sensor mounted in a tee. The term flowthrough is often taken to mean a conductivity sensor mounted in a sample sidestream. When provided with isolation valves, this mounting configuration is the most convenient because it allows the sample flow to be shut off and the sample line to be drained at will for maintenance and calibration. When sample conditioning is required, such as cooling, pressure reduction, or filtration and separation, this is the only configuration possible.

The major drawbacks to using a flowthrough sensor in a sample sidestream are the losses of process sample, unless sample return is provided, plugging of the sample line by solids or precipitates, and the possible lag time in getting the sample from the process to the sensor.

In general, choice of sensor mounting will be determined largely by the requirements of the process vessels and piping, as in the case of a pond or a sump, where the only mounting option is submersion. In other cases, there can be greater flexibility. Insertion mounting is most often the option of choice, because of its simplicity and low cost, but if sample cooling or pressure reduction is required, flowthrough mounting is the only option. Retraction or flowthrough mounting should be used in cases where it is necessary to access the conductivity sensor, while the process is running for cleaning or maintenance, especially when a reliable conductivity measurement is critical to the process. The added hardware and piping necessary for retraction and flowthrough mounting make the up-front cost greater than with insertion or submersion.

23.7 CONDUCTIVITY CALIBRATION

23.7.1 Calibration in Moderate to Highly Conductive Solutions

For conductivity measurements in excess of 50 μS/cm, a conductivity standard may be used to perform a single-point calibration on a conductivity loop, which is usually preceded by zeroing the analyzer with the sensor in air. The conductivity measurement may also be calibrated using a grab sample of the process. The following guidelines should be observed for grab sample standardization:

1. The grab sample should be taken near the online conductivity sensor, so the sample represents what the sensor is actually measuring.
2. The grab sample should be taken when the process conductivity and temperature are stable. Otherwise discrepancies can result from the grab sample not matching the process sample at the sensor. The online reading may not have fully responded to a change in conductivity, or the conductivity sensor may not have reached the process temperature.
3. Incorrect temperature compensation in the analyzer may show up as a discrepancy between the online and laboratory measurement.
4. If a chemical reaction is taking place in the process, the reaction may not have gone to completion at the online sensor, but will have by the time a grab sample reaches the laboratory.
5. The stability of the process sample is an important consideration. Some samples can react with air, or precipitate on cooling and change conductivity.
6. Grab sample standardization should never be used for conductivity measurements under 50 μS/cm. They are easily contaminated, especially in the case of high-purity water, which is almost immediately contaminated by carbon dioxide in ambient air.

Finally, it must be remembered that the laboratory or portable analyzer used to adjust the online measurement is not a primary conductivity standard. Errors in the laboratory or portable analyzer will result in an incorrect standardization of the online unit. Both the laboratory and online measurements can be checked with a primary conductivity standard, however.

23.7.2 High-Purity Water Measurements

Low-conductivity samples are highly susceptible to contamination by trace contaminants in containers and by CO_2 in air. As a result, calibration with a conventional standard is not possible. Any sample or grab sample taken would also be subject to the same contamination, and would be rendered unusable within seconds.

The alternative used by conductivity analyzers designed for high-purity water measurements is to calibrate the sensor input to the analyzer, using precision resistors. A conductivity sensor is used, which has an accurately known probe constant determined in a primary conductivity standard. Calibration of the analyzer and sensor combination is a simple matter of entering the probe constant into the analyzer. This feature is available only with microprocessor-based analyzers.

23.8 DIAGNOSTICS AND TROUBLESHOOTING

23.8.1 Traditional Error Detection and Troubleshooting

There are two categories of diagnostics: online and offline diagnostics. Online diagnostics alert the user to a problem in real time, during operation of the analyzer. Offline diagnostics are indications of a problem during calibration or maintenance of the sensor and analyzer.

A basic conductivity analyzer, is an analog device that simply transmits and displays conductivity. The only online indication of a problem is a conductivity reading that is obviously incorrect, based on what is known about the process. Troubleshooting is based on following a table of tests based on a description of the behavior of the conductivity signal online and during offline tests.

23.8.2 Analyzer Self-Diagnostics

Along with microprocessor-based conductivity analyzers came the ability to do more online diagnostic measurements and to show them on digital displays. These included self-checks of the microprocessor itself for malfunctions in the CPU and memory, but more importantly, included some checking of the input signals from the conductivity sensor. Input signal checking was able to detect open- or short-circuited temperature elements, and open circuits or short circuits in the sensor cable.

Offline diagnostics received a boost from the ability of the analyzer to calculate and display the probe constant on the basis of a calibration that had become an automated routine within the analyzer. It was now possible to note decreases in the probe constant, which indicate a coating problem. In fact, some analyzers calculate the probe constant from the first calibration, and calculate a correction factor, which gives an indication of coating or corrosion.

The most common catastrophic failure of a contacting or toroidal conductivity sensor is an open- or short-circuited temperature element, and, as noted, the analyzer checks this fault. Other failures that can occur are short circuits due to leakage of process into the sensor, and a sudden, abnormal amount of coating.

23.9 ANALYZER–USER INTERFACE AND OUTPUT SIGNAL

The user interface and output signals of a conductivity analyzer are the means by which the analyzer communicates with the user or a supervisory device. In describing each type of analyzer, the feature set of the analyzer determines what information is available, and the display and output signal determines where and how the information is made available. While the platforms described below roughly correspond to the historical development of conductivity analyzers, they are nevertheless all still currently commercially available (Table 23.1).

23.9.1 The Basic Analog Conductivity Analyzer

The basic conductivity analyzer is an analog device with zero and span adjustments (typically potentiometers) for zeroing and calibration. They have a very limited feature set, typically providing only a 4–20-mA output proportional to a conductivity range and a display (sometimes also optional in two-wire transmitters), either digital or analog, for displaying conductivity only. Line-powered units can include high/low-conductivity alarm contacts. These units, in most cases, lack the ability to accurately temperature compensate high-purity water. The major advantage of basic analog conductivity analyzers is their lower cost.

23.9.2 The Microprocessor-Based Conductivity Analyzer

Microprocessor-based conductivity analyzers offer a marked improvement over the basic analog devices. In terms of features, they typically include the ability to do high-purity water temperature compensation, and be calibrated for high-purity water, and may also include the ability to read out and be calibrated in concentration units. Software routines are included for configuration and calibration, which make the analyzer easier to use than the basic analyzer.

While the typical user interface consists of a keypad and display in all of these analyzers, the display types can vary from small LED or LCDs, which display nonnumerical information in three-character mnemonics, to larger displays capable of spelling out complete messages. To address the world market, the larger displays have become multilingual, although there is also an emerging trend toward symbolic, language-independent displays.

The output signal of these analyzers remains the analog 4–20-mA signal proportional to conductivity, with alarm contacts in the line powered devices. Line-powered devices may also include a second 4–20-mA output for a second conductivity range or a temperature. Line-powered units can use a dedicated alarm contact for remote indication of a diagnostic alarm, while two wire transmitters might use an overange 4–20-mA signal (21 or 22 mA) as an indication of a problem. Since all the diagnostic information resides in the analyzer, these remote signals are “come read” alerts to the user, who has to then go and interrogate the analyzer.

Table 23.1 Conductivity Analyzers

	Feature Set	User Interface	Remote Communication
Basic analog analyzer	Zero, span, and range adjustment Straight-line temperature compensation only	Analog or digital display of conductivity Potentiometers/ switches for zero, span, and range adjustment	4–20-mA signal proportional to conductivity Conductivity alarm contacts
Microprocessor-based analyzer	Temperature compensation for high-purity water and concentration measurements Special calibration routines for high-purity water and concentration measurements Calculation of concentration from conductivity Self-diagnostics	Digital display of conductivity, calibration constants, configuration parameters, and error messages Software routines for calibration and configuration Keypad for entering numerical values and navigating among software routines	4–20-A signal proportional to conductivity Conductivity alarm contacts Fault alarm via alarm contact or overange 4–20-mA signal
Smart conductivity analyzer	Temperature compensation for high-purity water and concentration measurements Special calibration routines for high-purity water and concentration measurements Calculation of concentration from conductivity Self-diagnostics	Digital display of conductivity, calibration constants, configuration parameters, and error messages Software routines for calibration and configuration Keypad for entering numerical values and navigating among software routines	Digital conductivity signal (also 4–20-mA signal in some cases) Digital conductivity alarms (also pH alarm contacts in some cases) Digital fault messages (also fault alarm contact in some cases) Full access to the instrument for calibration and configuration via a handheld remote terminal, PC, or host control system

23.9.3 Smart Conductivity Analyzers

Smart conductivity analyzers combine the features of the microprocessor-based analyzer with “smart,” digital communications. This not only allows diagnostic information to be transmitted to a remote location along with the conductivity measurement but also makes it possible to interrogate, configure, and even calibrate the analyzer remotely. There are a number of protocols available for smart communications, a number of which are manufacturer specific. No protocol has, as yet, become a standard in the same way that the 4–20-mA analog signal has. The most widely used protocols for analyzer are HART, Modbus, FOUNDATION Fieldbus, and Profibus. Smart analyzers are more costly than the general microprocessor-driven analyzers.

To access the digital information provided by the analyzer, the user needs a communication device, which can take the form of a handheld keypad display for configuration and calibration in the field, a PC, or a host control system. The use of a PC for communication with smart conductivity analyzers has led to the development of maintenance software packages that provide a software environment for configuration, troubleshooting, and calibration. These software packages can include a database for recording timestamped error messages and calibration data, thus automating the task of keeping maintenance records.

23.10 APPLICATION OF CONDUCTIVITY

23.10.1 Nonspecific Applications

Nonspecific applications involve simply measuring conductivity to detect the presence of a certain bulk concentration of electrolytes, that is, there is no attempt to derive the concentration of a particular electrolyte from the measurement. The majority of conductivity applications fall within this category. They include monitoring and control of demineralization, leak detection, and monitoring to a prescribed conductivity specification, as in the case of power generation equipment. In most instances, there is a maximum acceptable concentration of electrolyte, which is related to a conductivity value, and that conductivity value is used as an alarm point.

23.10.1.1 Interface Detection. An often over looked application of conductivity is in detecting the interface between a conductive solution and a nonconductive solution. The nonconductive solution can be a solvent or hydrocarbon, and the conductive solution can be virtually any water sample. The principle is simple: There is some upscale conductivity reading in the water solution and no conductivity reading in the nonconductive solution. The conductivity output is used to provide an on/off signal to indicate which phase the sensor is in. This application almost always employs a toroidal conductivity sensor, because solutions of solvents and hydrocarbons can foul an electrode sensor.

23.10.2 Leak Detection with Conductivity

Conductivity can be used to detect the leak of more conductive contaminant into a less conductive sample. The greater the difference in conductivity is between the contaminant and the sample, the greater the sensitivity of leak detection will be.

In general, unless the contaminant is at least 100 times more conductive than the sample, the sensitivity of leak detection will be poor.

An approximation of the fractional change in conductivity accompanying a leak can be calculated as follows: $F = (V_C/V_S)\ (C_C/C_S)$, where F is the fractional change in conductivity; V_C and V_S are the volumes (or flow rates) of the contaminant and the sample, respectively; and C_C and C_S are the conductivities of the contaminant and the sample, respectively. The minimum leak detectable will be the volume or flow rate of contaminant, which gives a conductivity change over the normal sample conductivity that can be reliably measured by the analyzer. The minimum leak detectable will depend on the accuracy of the conductivity measurement and the extent to which the conductivity of the sample normally varies.

Where the sample conductivity varies over time, the maximum conductivity of the sample should be used for estimating the sensitivity of leak detection. In some cases, two conductivity measurements can be used before and after the source of a potential leak and the difference between the two reading used to detect a leak. The accuracy of the conductivity measurements and the normal changes in sample conductivity over time will determine the minimum conductivity difference, which can be used for alarming.

23.10.3 Concentration Measurements

Conductivity is nonspecific, but it can sometimes be applied to concentration measurements if the composition of the solution and its conductivity behavior are known. The first step is to know the conductivity of the solution as a function of the concentration of the electrolyte of interest. These data can come from published conductivity–concentration curves for electrolytes, or from laboratory measurements. The conductivity of mixtures usually requires a laboratory measurement due to the scarcity of published conductivity data on mixed electrolytes.

Over large concentration ranges, conductivity will increase with concentration, but may then reach a maximum and then decrease with increasing concentration. It is important to use conductivity data over the temperature range of the process, because the shape of the conductivity–concentration curve will change with temperature, and a concentration measurement may be possible at one temperature but not another.

23.10.3.1 Necessary Conditions. With the conductivity versus concentration data in hand, it can be reviewed for the two necessary conditions for a concentration measurement:

1. There must be a measurable change in conductivity over the desired concentration range.
2. Conductivity must either strictly increase or decrease with increasing concentration. If a maximum or a minimum is present in the of conductivity–concentration curve, in the desired concentration range, concentration cannot be measured over concentration ranges containing these extreme points (Fig. 23.9).

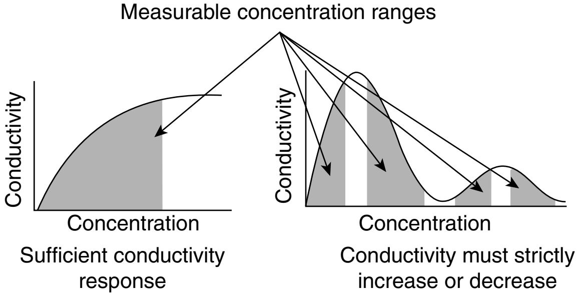


Figure 23.9 Conductivity–concentration plot.

23.10.3.2 Cases Where Concentration is Measurable. If the two necessary conditions are met, concentration can be measured in each the following cases:

1. The solution is a single electrolyte in solution, or the conductivity of other solution components is very low.
2. The conductivity due to other electrolytes is large relative to the electrolyte of interest, but their concentration remains constant.
3. The concentration of a mixture of electrolytes and any one or all of its components can be measured, if their ratio remains constant (e.g., a detergent solution).

23.10.3.3 Concentration Analyzers Based on Conductivity. Many conductivity analyzers include an output option for displaying and transmitting the concentration of a particular electrolyte over a specified concentration range. This is great convenience to users over having to develop their own concentration applications. As these concentration measurements are conductivity-based, the principles outlined above apply to them as well. The concentration ranges chosen are those where the conductivity strictly increases or decreases with increasing concentration, within specified temperature limits. Samples with concentrations outside the specified concentration or temperature range will give erroneous readings, which can appear believable. For this reason, it is important to apply these analyzers only within the specified ranges.

The algorithms used in concentration analyzers are based on the conductivity curve of the pure electrolyte in solution. Therefore they are applicable only to samples consisting of the pure electrolyte, or samples with negligible background conductivity. A common error is to apply these analyzers to samples that have a significant concentration of other electrolytes. The concentration reading will be erroneous, but can appear to be the true concentration. The sample composition must be known and evaluated before these analyzers are applied.

23.10.4 Reaction Monitoring and Endpoint Detection

Chemical reactions, typically batch reactions, in electrolyte solutions can be accompanied by conductivity change sufficient to allow their progress to be followed by conductivity. Potential applications can be evaluated by measuring the conductivity at various stages in the reaction and relating it to a laboratory analysis of the reaction mixture at each stage. Conductivity can be related to the percent completion of the reaction or to the concentration of any reactant or product.

23.11 SUMMARY

When properly applied, online conductivity is probably the most straightforward and lowest maintenance of all online analytical measurements. While conductivity can be applied to the full range of water solutions, from high-purity water to the most conductive solutions known, the key to a successful application is knowing the sample's conductivity characteristics and applying the correct technology. These can be outlined as follows:

- Use toroidal conductivity for dirty, corrosive, or high-conductivity applications.
- For accuracy in applications approaching 1 μS/cm, use electrode conductivity and an analyzer with high-purity water temperature compensation.
- Use contacting conductivity for low-conductivity applications in clean process streams.

In many cases, conductivity is used as a nonspecific measurement, with a high alarm point based on a prespecified conductivity limit. Conductivity may also be applied with a specific analysis goal in mind. If leak detection is the goal of the application, the conductivity range of the sample and contaminant must be known, as well as an estimate of the overall measurement accuracy. Applying conductivity to concentration measurements requires the conductivity of the sample over the concentration and temperature range to be known. Following a chemical reaction with conductivity must be based on a laboratory analysis of the sample composition and its conductivity at various stages in the reaction.